CHEMICAL EQUILIBRIUM AND KINETIC STUDY OF THE ESTERIFICATION OF ACRYLIC ACID WITH BUTANOL CATALYSED BY SULFONATED EXPANDED POLYSTYRENE

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ABSTRACT

The wastewater containing low concentration (4-10 wt %) of acrylic acid (AA) was treated by incineration since it is very toxic to the organism if it is discharged to the environment. This valuable compound can be recovered using one of the promising methods, the esterification of the diluted AA with alcohol. The sulfonated expanded polystyrene (SEP) from waste expanded polystyrene is a good catalyst to catalyse the esterification of AA with butanol (BuOH). The production of this catalyst can have high impact in environment since the waste polystyrene is huge environmental issues. The SEP was synthesised via the sulfonation of waste expanded polystyrene using sulphuric acid (H_2SO_4) at 378 K. The slurry obtained after 2 hour of sulfonation was transferred into water and washed with sodium hydroxide, acid hydrochloric and excess water before dried at 343 K. The SEP has a rough surface with minute cracks, can withstand up to 403 K and density of 1.2790 g/cm^3. The swelling effect in SEP helps the reactant access the active sites. The activity and kinetic study for this esterification reaction was carried out in batch system. The effect of various parameters that affecting conversion and yield such as stirring speed, initial molar ratio of AA to BuOH, catalyst loading, temperature and initial water content were studied. The reaction was more sensitive to temperature as compared to other parameters. The best conversion and yield obtained at molar ratio AA to BuOH of 1:3, catalyst loading of 10 wt% and temperature of 353 K were 92% and 75% respectively. The yield of butyl acrylate decrease with the increase of initial water content in the reaction mixture because water shifts the reaction equilibrium to reactants, blocked the reactants from accessing active sites and increase polymerisation on the SEP surface. Nevertheless, the SEP can be regenerated easily using sulphuric acid. The experimental kinetic data was correlated to the several kinetic models which were pseudo-homogeneous (PH), Eley-Rideal (ER) and Langmuir Hinshelwood Hougen Watson (LHHW) model. The activation energy is 73.6 kJ/mol. The best fitted model for the main esterification reaction was shown by the non-ideal ER I model. Taking the polymerisation into account, the experimental data are more comparable with the predicted data.

ABSTRAK

Air sisa yang mengandungi kepekatan asid akrilik (AA) yang rendah iaitu dalam lingkungan 4 hingga 10 berat% dirawat dengan pembakar kerana bertoksik kepada organisma jika dilepaskan ke alam sekitar. AA dalam air sisa ini, boleh diperoleh semula melalui proses pengesteran dengan alkohol. Polisterina tersulfonasi (SEP) yang dihasilkan daripada polisterina terpakai adalah pemangkin yang bagus untuk pengesteran AA dengan butanol (BuOH). Penghasilan pemangkin ini boleh memberi impak yang besar kerana polisterina terpakai adalah salah satu penyumbang terbesar kepada masalah alam sekitar. SEP ini dihasilkan melalui proses sulfonasi antara polisterina terpakai dengan asid sulfurik pada suhu 378 K. Selepas 2 jam proses sulfonasi, buburan dipindahkan kedalam air dan dibasuh dengan larutan natrium hidroksida, asid hidroklorik dan air sebelum dikeringkan pada suhu 343 K. SEP yang dihasilkan berketumpatan 1.2790 g/cm^3. Ia mempunyai rekahan dan permukaan yang kasar dan mampu bertahan sehingga suhu 403 K. Kesan pembengkakan dalam SEP membantu bahan tindak balas bergerak ke tapak aktif dengan lebih mudah. Kajian terhadap aktiviti dan tindak balas kinetik terhadap pengesteran dilakukan dalam reaktor kelompok. Pelbagai parameter yang mempengaruhi kadar tindak balas antaranya kadar kacauan, nisbah awal mol antara AA dan BuOH, muatan pemangkin, suhu dan kandungan awal air dalam bahan tindak balas telah dikaji. Tindak balas pengesteran adalah lebih sensitif terhadap suhu berbanding parameter yang lain. Kadar terbaik penukaran AA dan penghasilan butil akrilik (BA) pada nisbah mol 1:3 antara AA dan BuOH, muatan pemangkin sebanyak 10 berat%, dan suhu 353 K adalah 92% dan 75%. Penghasilan butil akrilik berkurang dengan kandungan awal air dalam campuran bahan tindak balas kerana air telah menganjakkan keseimbangan tindak balas ke bahan tindak balas, menghalang bahan tindak balas daripada mencapai tapak aktif, dan meningkatkan kadar pempolimeran diatas permukaan SEP. SEP juga mudah di jana semula dengan asid sulfurik. Data kinetik eksperimen telah di kaitkan dengan beberapa kinetik model iaitu model pseudo-homogeneous (PH), model Eley-Rideal (ER) dan model Langmuir Hinshelwood Hougen Watson (LHHW). Tenaga pengaktifan yang dikira adalah 73.6 kJ/mol. Model yang terbaik untuk tindak balas pengesteran adalah model bukan ideal, ER I. Dengan mengambil kira pempolimeran, data eksperimen adalah lebih serasi dengan data jangkaan.

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LIST OF SYMBOLS

A	Acid
α_i	Activity coefficient of component *i*
E_f	Activity energy of reaction
K	Adsorption constant
B	Alcohol
K_x	Apparent equilibrium constant
Φ	Association parameter
Rc	Catalyst radius
R^2	Coefficient of determination
C_i	Concentration of component *i*
ρ	Density
D_{AB}	Diffusivity
D_{eff}	Effective diffusivity
K_{eq}	Equilibrium constant
X_e	Equilibrium conversion
E	Ester
k_f	Forward rate constant
γ_i	Gamma of component *i*
R	Gas constant
b_i	*i*th adjustable parameter
K	Kelvin

C_{li}	Limiting concentration
K_c	Mass transfer coefficient
M	Molarity
M	Molar ratio
x_i	Mole fraction of component *i*
m	Number of adjusted parameters
d_p	Particle diameter
%	Percent
K_{fo}	Pre-exponential factor
n	Reaction order
r_i	Reaction rate of component *i*
P/P_o	Relative pressure
rpm	Revolution per minute
N_{sc}	Schmitt Number
σ	Standard deviation
Δ	Standard enthalpy of reaction
T	Temperature
K_a	Thermodynamic equilibrium constant
V	Volume
ε	Void fraction
μ	Viscosity
W	Water
wt	Weight

LIST OF ABBREVIATIONS

AA	Acrylic acid
BuOH	Butanol
BA	Butyl acrylate
COD	Chemical oxygen demands
CSZ	Conventional sulphated zirconia
ER	Eley-Rideal
EPS	Expanded polystyrene
FID	Flame ionization detector
FT-IR	Fourier Transform spectroscopy
GC	Gas chromatography
HPA	Heteropolyacids
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
IEC	Ion exchange capacity
LHHW	Langmuir Hinshelwood Hougen Watson
MCMC	Markov chain Monte Carlo
C_M	Mears criterion
MSZ	Mesoporous sulphated zirconia
NA	Not available
OFAT	One factor at a time
PBLR	Packed bed loop reactor

PH	Pseudo-homogeneous
RDC	Reactive distillation column
SEM	Scanning electron microscopy
SMBR	Simulated moving bed reactor
SDP	Sodium dihydrogen phosphate
SEP	Sulfonated expanded polystyrene
TMA	Tetravalent metal acid
TGA	Thermogravimetric analysis
TPA	Tungstophosphoric acid
UNIFAC	Universal functional activity coefficient
UASB	Upflow anaerobic sludge blanket
WCO	Waste cooking oil
C_{WP}	Weisz-Prater criterion
ZCO	Zirconium chloride octahydrate

CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

Acrylic acid (AA) is commercially important in chemical industry and it is widely used for the production of acrylic esters which are applied in surface coating, textiles, adhesives, paper treatment, polishes, leather, fibre, detergents and super-absorbent material (Xiaobo *et al*., 2006, and Altiokka and Ödeş, 2009). AA is very toxic to aquatic organism and its' release to the effluents should be minimised (Bajt *et al.,* 1997 and Staples *et al.,* 2000).

Wastewater containing AA (1.8-20 g/l) exhibits high chemical oxygen demand (COD) content which renders direct biological treatment of this water takes extremely long time and requires reactor with high capacity (Stewart *et al*., 1995 and Chen *et al*., 2008). This wastewater is burned in most of the AA production plant using incinerator which is rather expensive and not environmental friendly (Allison *et al.*, 2011). Several methods such as adsorption and wet oxidation were used to remove AA in the diluted system. Even though both of these methods could remove AA for >98%, its applications are only limited to the wastewater containing AA of 50 to 500 mg/l for adsorption and 1000 to 4000 mg/l for wet oxidation (Silva *et al*., 2003 and Kumar *et al.,* 2010). Distillation and extraction are the conventional methods used to recover AA. These methods consumed substantial energy and suffer with phase separation limitation. Esterification can recover diluted acid by converting the acid to the valuable ester (Arpornwichanop *et al*., 2008). The same idea exploited by Saha *et al.* (2000) and Bianchi *et al*. (2003) for the recovery of diluted acetic acid. The equilibrium condition of the esterification reaction can be shifted towards products by continuously removing

the products from the reactant mixture. The combine reaction and separation in a single column has saved energy, increased conversion and avoided catalyst poisoning particularly in the aqueous system (Tuchlenski *et al.,* 2001; Omota *et al*., 2003 and Schimtt *et al*., 2004).

1.1 PROBLEM STATEMENT

Esterification of AA with alcohol (butanol, ethylhexanol and propylene glycol) produces acrylates by direct acids catalysed esterification at elevated temperature. This process is a reversible process (Chen *et al*., 1999; Altiokka and Ödeş 2009; Ostrowski *et al.,* 2011 and Komoń *et al.,* 2013). Homogeneous catalyst is used in the conventional method to accelerate the esterification reaction which consuming days to achieve equilibrium. Strong liquid mineral acids such as sulphuric acid, hydrochloric acid, hydrogen iodide and *p*-toluenesulfonic acid have been used for industrial esterification reaction. In spite of the strong activity of these homogeneous catalysts, it imposed several drawbacks such as corrosion problems, difficult to be separated from the reaction mixture and necessity to be neutralized after reaction (Lilja *et al.*, 2002; Jermy and Pandurangan, 2005; Liu *et al*., 2006; Peters *et al.,* 2006, and Akbay and Altiokka, 2011). Heterogeneous catalyst has been developed to overcome the aforementioned shortcomings. In addition, heterogeneous catalyst also can suppress the side reactions (Rattanaphra *et al*., 2011, and Akyalçin and Altiokka, 2012).

Ion exchange material is widely used as heterogeneous catalyst for the esterification reaction because of its special characteristics such as insoluble, good selectivity and specificity (Blagov *et al*., 2005 and Park *et al.*, 2009). The sulfonated expanded polystyrene (SEP) is an ion exchange catalyst which contains high ion exchange capacity and high accessibility to acid sites (Grossi *et al.,* 2010). The catalyst also is inexpensive because can be synthesised from the waste polystyrene (Bekri-Abbes *et al.,* 2008).

In view of the environmental and economic impacts of the wastewater containing AA, practicability of the recovery of AA from wastewater through

esterification should be investigated. A suitable water tolerance heterogeneous catalyst should be identified prior to aqueous esterification and process study.

1.2 OBJECTIVES

In the present work, esterification of pure and diluted acrylic acid with butanol was studied with the objectives of:

1. To synthesise, screening and characterise the suitable heterogeneous catalysts.
2. To study the effect of different important operating parameters.
3. To develop the kinetic model for the reaction.

1.3 SCOPES OF STUDIES

1. The catalysts include SEP, Amberlyst-15, sulphated zirconia, molybdenum zirconia, zirconium phosphate, sulfonated carbon, and zeolite ZSM 5 were tested.
2. The SEP was characterized using scanning electron microscopy (SEM) thermal gravimetric analysis (TGA), Fourier transform spectroscopy (FT-IR) and gas pycnometer.
3. The effect of important operating parameters such as stirring speed, reactant molar ratio, temperature, catalyst loading, reusability and initial water content were investigated.
4. The kinetic study was carried out and fit to different types of model such as Eley-Rideal (ER) model, Langmuir Hinshelwood (LHHW) model and pseudo-homogeneous (PH) model.

1.4 SIGNIFICANCE OF STUDY

Study on the esterification of wastewater containing AA with butanol would contribute to the development of a feasible AA recovery method from the wastewater. Wastewater could be treated while producing value added esters. This method is expected to overcome the economic and environmental problems faced by the existing

method such as incineration. Moreover, additional income could be generated through the value added product. The present study also would contribute to the discovery of a water tolerance heterogeneous catalyst for esterification of acrylic acid with water.

1.5 ORGANISATION OF THE THESIS

The subsequent sections of the thesis comprise of chapter 2 (literature review), chapter 3 (methodology), chapter 4 (results and discussion) and chapter 5 (conclusions and recommendations).

Chapter 2 includes the review about the existing treatment methods for the wastewater containing carboxylic acid particularly acrylic acid. The literature also focuses on the potential of AA recovery via the esterification reaction followed by the comparison on the performance of difference types of catalyst. The relevant kinetic models are included.

Chapter 3 describes the materials, apparatus and equipment used to synthesise and characterise the catalyst. The procedures for the catalyst synthesis, catalyst characterisation, catalyst activity testing and the reaction product sample analysis are also delineated in detail.

The results obtained in the present research are discussed accordingly to the following sequence in results and discussion chapter: (1) Catalyst screening, (2) Catalyst characterisation, (3) Studies about the effect of important operating parameters, (4) Equilibrium studies using the best catalyst in the esterification of AA with butanol and (5) Kinetic studies.

In the conclusions and recommendations, conclusions are drawn based on the research findings. Recommendations are suggested to improve the future research work in related area.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

This chapter reviews on the methods used to treat wastewater containing AA and the potential methods to recover AA from the wastewater. There are also reviews on the type of catalysts used for the esterification reaction, particularly on the AA esterification. The corresponding kinetic models were reported for the heterogeneously catalysed AA esterification reaction.

2.1 ACRYLIC ACID

Acrylic acid (AA) has several synonyms names which are propionic acid, acroleic acid, ethylene carboxylic acid and vinyl formic acid. AA is a clear colourless liquid, fuming, and corrosive with acrid odour. AA tends to spontaneous polymerise which can be explosive in confined space. The best storage is above melting point to avoid crystallisation. Table 2.1 summaries the physical properties of AA.

Table 2.1: Physical properties of AA

Property	Acrylic acid
Molecular weight	72.06
Density (g/ml) at 298 K	1.045
Melting point (K)	286
Boiling point (K) at 101 Kpa	414
Vapour pressure (kPa) at 298 K	0.57
Heat of polymerization (kJ/mol)	76.99
Refrective index	1.4185
Critical temperature	615K
Critical pressure (bar)	56.6
Critical volume (cm^3/mol)	208
Accentric factor	0.538
Solubility in water and alcohol	miscible

Source: Kricheldorf, 1991; Ostaniewicz-Cydzik *et al.,* 2014

The demand of AA and its derivatives is increasing as they are the basic building blocks for chemical industry especially for polymeric products. The acrylates are intermediate products of high commercial value due to its properties such as excellent clarity, elasticity, colour retention toughness, easy adhesion, chemical inertness and UV stability. The current production of AA in the petrochemical industry involves two-step gas phase oxidation of propylene. The worldwide productivity of AA in 2003 was more than 3 million tons per year. The production increased to 4.7 million tons in 2006. The global demand was estimated to increase 4.8% per year from year 2010 until 2015.

Half of the production is for acrylates, where approximately 60% is for production of butyl acrylate, BA. The acrylates are used in fiberfill bonding, textile bonding or laminating, flocking, back coating, pigment printing binders, leather finishing, adhesives, super-absorbent materials, detergents and varnishes (Saha and Sharma, 1995; Xiaobo *et al*., 2006; Altiokka and Ödeş, 2009; Ortrowski *et al*., 2011 and Niesbach *et al*., 2013). AA are readily absorbed and rapidly metabolized and excreted primarily as carbon dioxide. Inhalation or exposure from polishes, paints, coating, rug backing, adhesives, plastics, textiles, and paper finish acrylic acids is irritating to the eyes, skin, and respiratory system (Idriss, 2002).

2.2 TREATMENT METHODS OF WASTEWATER CONTAINING CARBOXYLIC ACID

In an acrylic manufacturing unit, the typical wastewater contained 10-20 g/l of acrylic acid, whereas the wastewater from the related petrochemical manufacturing unit contained relatively low concentration of AA (1.8 g/l) (Schonberg *et al.,* 1997 and Kumar *et al*., 2010). Although the AA is in low concentration, is very toxic to living things especially aquatic organism. AA is severely irritates skin, eyes, respiratory system and gastro-intestinal tract of the human being (Idriss, 2002; Silva *et al.,* 2003 and Kumar *et al*., 2009). The low concentration of AA in wastewater complicates its recovery and treatment processes. The common industry practice used to destruct the wastewater containing AA is by burning it in a chemical incinerator equipped with after burner and scrubber (Vincolli, 1996).

2.2.1 Biological Treatment

Recovery of organic chemicals is desirable from the view point of green chemistry but it is difficult since the AA concentrations are very low in the wastewater. Activated sludge is used to remove the organic compound from the wastewater. These organic compounds are carbon source for the microbe metabolism which would be converted to carbon dioxide (CO_2) and excess activated sludge. The excess sludge is incinerated to generate CO_2 (Igarashi *et al*., 2012). Activated sludge relies in the self-assembly of an active microbial which can form flocculants aggregates and separated from effluent by gravity settling. The bacteria are dominant to remove oxygen-demand pollutants and bacterial compositions are not affecting the system (Ibarbalz *et al*., 2013).

Anaerobic digestion, another method under biological treatments degrades and stabilises the organic materials under anaerobic condition by microorganism which producing carbon dioxide and methane. This process uses low energy, due to its ability to recover energy. It does not produced substantial amount of sludge. The wastewater containing AA can be treated with *Arfhrobacter sp*. strain NO-18 because of its capability to grow with solely acrylic acid as a carbon source. However, the system has low operational stability (Schonberg *et al*., 1997 and Chen *et al*., 2008). Stewart *et al.*

(1995) studied on the treatment of wastewater containing acrylic acid with the concentration of 100 to 1500 mg/l using glucose-acetate enrichment culture with volatile suspended solid ranging from 2275 to 2625 mg/l. The acrylic acid can be degraded to less than 1 mg/l (>99%) in 40 days.

Demirer and Speece (1998) studied on the anaerobic treatment of diluted acrylic acid in a single stage upflow anaerobic sludge blanket (UASB) reactor using *Methanosarcina* culture. The influent with the AA concentration of 3000 mg/l bio-transformed into intermediate product (acetic acid and propionic acid) at 95% efficiency after 103 days at a loading rate of 2.7 g/l/day and a hydraulic retention time (HRT) of 26 hours. The COD removal was 45%. The COD removal increased to 97% when double stage UASBs was used.

Synthetic wastewater (85 g/l of COD) containing 0.66% of AA and other components were treated in an anaerobic membrane reactor with the loading at 1 L/day and HRT of 25 days. The COD reduced to 0.6% of COD influent. This reactor showed excellent removal of AA (~100% efficiency) and the volatile organic matter in the wastewater was degraded and converted into methane (Bhattacharyya *et al.,* 2013). The conventional biological treatment method (activated sludge) required extremely long residence time to retain the growth of the organism and large vessel for high reactor capacity. The process efficiency of the biological system was limited by biomass concentration and hydraulic retention time. The biomass concentration was very low due to the diluted wastewater (Chen *et al.,* 2008). The limitation of AA concentration was 100 mg/l for anaerobic treatment that used methanogenic cultures because higher concentration will inhibit the cultures and reduced the performance (Demirer and Speece, 1998 and Huang *et al.,* 2014).

2.2.2 Adsorption

Adsorption is an interracial phenomenon controlled by the nature of the absorbent, absorbate and the solution chemistry. This process is simple operation that operating at operates at ambient temperature and pressure. In the water and wastewater treatment, adsorption using activated carbon is a commonly used treatment method due

to high surface, high degree of surface activity, large pore volume and excellent efficiency for organic compound (Duan *et al.*, 2002; Oneto *et al*., 2004; Chai and Ji, 2012; Cabrera-Lafaurie *et al.,* 2014 and Khan *et al.,* 2014). Kumar *et al*. (2009) studied on the potential of powdered activated carbon for the adsorption of AA in aqueous solution (50-500 mg/l). The maximum adsorption was 36.23 mg/g with optimum dosage of 20 g/l for the initial concentration of 100 mg/l. The removal of AA was >84% within 5 minutes contact time and the residual of approximately 1.6% of the initial concentration. The equilibrium data and kinetic data followed Freundlich isotherm and pseudo-second order model respectively. The adsorption of AA was influenced by the decrease of temperature. Mao and Fung (1997) also studied on adsorption of aqueous AA (0.1 M) using alumina as adsorbent. The studies found that the adsorption of AA on alumina depended on the pH and obeyed Langmuir isotherm which showing the dependence of the adsorption on active surface area and surface chemistry of the adsorbents. At optimum pH (4.5), the maximum adsorption was 727 μmol/g and the equilibrium at 48 hours (100% of plateau value). The adsorption treatment method is only economic and feasible for the wastewater containing minute amount (<500 ppm) of AA (Xu *et al.,* 2013).

2.2.3 Wet Oxidation

Wet oxidation is also known as subcritical hydrothermal oxidation for wastewater effluent which is too dilutes for incineration and too concentrated or toxic for biological treatment (Oneto *et al*., 2004). Catalyst is the key factor in wet oxidation since AA is thermally stable (553 K) and poorly oxidised below 523 K.

The pressurised reactor was injected 1000 ppm of AA with 6 g/l of catalyst loading, oxygen partial pressure of 15 bar and 350 rpm. Different metal oxide used as catalyst with cerium oxide as support at a molar ratio of 70:30. The highest efficiency of oxidation process was 97.7% using manganese/cerium followed by argentums/cerium (85%) and cobalt/cerium (65.1%) (Silva *et al*., 2003). Kumar *et al*. (2006) also studied the cerium based catalyst for wet oxidation of diluted AA with the concentration of 5 g/l of AA at different temperatures. The manganese (Mn) and cerium (Ce) was equal to molar. The catalyst loading was 5 g/l and airflow rate was maintained at 0.25-0.3 LPM.

The maximum removal under atmospheric pressure was only 16% after 30 hours at 368 K comparing to the pressurised reactor (14 kg/cm^2) which achieving 86.12% COD reduction after 6 hours at 453 K. Oliviero *et al*. (2000) studied the ruthenium supported on cerium for the treatment of aqueous solution of AA (52 mmol/l) at 433 K and 20 bar for 3 hours. This ceria gave high surface area to insure oxygen activation when AA was adsorbed. The conversion of AA was 100%. The conversion of AA into formic acid and acetic acid did not exceed 40% for the carbon supported catalyst because the low AA adsorption affinity. The wet oxidation treatment is an effective for wastewater containing AA with 2-50 g/l of COD. However, it requires elevated temperature to maintain its high removal efficiency.

2.2.4 Esterification

The treatment methods for wastewater containing AA with various concentrations such as biological treatment, adsorption and wet oxidation have shown the respective shortcomings despite its high efficiency. Furthermore, some of these methods are not appropriate for the targeted wastewater containing AA with the concentration of 4-10 wt%. The limitation of these methods was included in Table 2.2. Esterification of the wastewater containing carboxylic acid with alcohol has been reported as a promising to convert carboxylic acid to a valuable product while purifying the wastewater (Bianchi *et al.,* 2003 and Ragaini *et al.,* 2007).

CHAPTER 1

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2. The SEP was characterized using scanning electron microscopy (SEM) thermal gravimetric analysis (TGA), Fourier transform spectroscopy (FT-IR) and gas pycnometer.
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1.4 SIGNIFICANCE OF STUDY

Study on the esterification of wastewater containing AA with butanol would contribute to the development of a feasible AA recovery method from the wastewater. Wastewater could be treated while producing value added esters. This method is expected to overcome the economic and environmental problems faced by the existing

CHAPTER 3

RESEARCH METHODOLOGY

3.0 INTRODUCTION

The present chapter includes the materials, apparatus, and equipment used for the catalyst synthesis, characterisation and catalytic activity testing throughout the study of the esterification of the pure and dilute acrylic acid with butanol. All the experimental procedures are also delineated.

3.1 MATERIALS

The chemicals used in the present study are listed in the Table 3.1 with its brand, purity, and functions. All these chemicals were used without further purification.

Table 3.1: List of chemical

Chemicals	Assay (%)	Supplier	Function
1-butanol	99.8	Sigma Aldrich	As a reactant
Acrylic acid	99	Aldrich	As a reactant
Amberlyst 15	NA*	Sigma Aldrich	catalyst
Ammonium molybdate tetrahydrate	81-83	Merck	As a reactant for catalyst synthesis
Argentums nitrate	99.8	R&M chemicals	As an indicator
Barium chloride	100.02	Fisher	As an indicator
Butyl acrylate	≥99.5(GC)	Fluka	As a standard for GC-FID analysis
Compressed Air	99.99	Air product	To initiate flame in FID
Helium gas	99.99	Air product	As a mobile phase and carrier for GC-FID analysis
Hydrochloric acid	37	Merck	As a reactant for catalyst synthesis
Hydrogen gas	99.99	Air product	As an inert gas for GC-FID
n-hexane	98	Merck	As a solvent for GC-FID analysis
Nitric acid	65	R&M chemicals	As a reactant for catalyst synthesis
Nitrogen gas	99.99	Air product	As a makeup for GC-FID
Phenolphthalein	NA*	Emory Laboratory Chemicals	As an indicator
Potassium hydrogen phthalate	99.5	Merck	For standardise KOH solution
Potassium hydroxide	85	Merck	For IEC analysis
Sodium chloride	100.1	Fisher	For IEC analysis
Sodium dihydrogen phosphate	99	Systerm	As a reactant for catalyst synthesis
Sodium hydroxide	99	R&M chemicals	As a reactant for catalyst synthesis
Starch		Sigma Aldrich	As a reactant for catalyst synthesis
Sulphated zirconia	NA*	NA*	Catalyst
Sulphuric acid	96	Fisher	As a reactant for catalyst synthesis
Waste expanded polystyrene	NA*	NA*	As a reactant for catalyst synthesis
Zirconium hydroxide	97	Aldrich	As a reactant for catalyst synthesis
Zirconyl chloride octahydrate	98	Sigma Aldrich	As a reactant for catalyst synthesis
ZSM-5 zeolite	NA*	Alfa Aesar	catalyst

*NA denotes not available

3.2 APPARATUS AND EQUIPMENT

3.2.1 Catalyst Characterisation

The sulfonated expanded polystyrene (SEP) were examined using Scanning Electron Microscopy (SEM), thermogravimetric analyser, Fourier Transform Infrared Spectroscopy (FT-IR) and gas pycnometer for its morphology, thermal stability, functional groups and density.

3.2.2 Esterification Reaction Studies

The catalysts were tested through esterification reaction carried out in a three necked flask equipped with condenser, temperature controller and temperature probe. Figure 3.1 shows the experimental setup and Table 3.2 shows the function of each part in the set up.